SYNOPSIS

(1) TITLE OF THE SYNOPSIS

"PHYSICOCHEMICAL STUDIES OF SOME MONOMERIC AND GEMINI SURFACTANTS AND THEIR INTERACTIONS WITH SERUM ALBUMIN PROTEINS "

(2) INTRODUCTION

The protein-surfactant interactions have been a subject of extensive studies due to wide variety of industrial, biological, pharmaceutical and cosmetic applications [1-3]. Protein-surfactant interactions have been explored the effect of surfactants on structure of protein in the form of solubilization and denaturing or renaturing of protein [4-5]. Globular proteins are frequently used as functional ingredients in healthcare and pharmaceutical products, due to their ability to catalyze biochemical reactions, to be adsorbed on the surface of some substance and to bind other moieties and form molecular aggregates. One of the most widely used globular protein is bovine serum albumin (BSA), since it has a well-known primary structure and been associated with the binding of many different categories of molecules, such as dyes, drugs and toxic chemicals [6-7].

Protein exhibits dualism because of the hydrophobic and hydrophilic properties of the amino acids that causes amphiphilic molecules to interact with it. In general, the amphiphilic molecules chosen for the study of protein-surfactant interactions are ionic surfactant in view of their application in the area of membrane study [8-9]. Cationic surfactants interact with proteins to a lesser extent as compared to the anionics because of the small relevance of electrostatic interactions at the pH values of interest. However, the shape of binding isotherms of both of the surfactants have been found to be similar [10].

Protein-surfactant interactions are usually dependent on the surfactants features. Surfactants are characterized by properties such as the critical micelle concentration (CMC), chemical structure and charge as well as by source. Physicochemical properties of surfactants are significantly influenced by the presence of additives. Surfactants of both biological and chemical

origin are amphiphatic molecule that accumulates at interface, decrease interfacial tension and form aggregate structure such as micelles [11-15]. Chemical surfactants are available in many forms and are generally classified based on charge as anionic, cationic, non-ionic and amphoteric [16-17].

Most of the research paper has been focused on single-chain surfactants. More recently, several reports have been discussed the unique behaviors of the interaction between protein and gemini surfactants [18-19]. Gemini surfactants are consists of two amphiphilic molecules connected at the level of head groups by a spacer. A large number of studies have focused on the development of gemini surfactants as these kinds of surfactant have a number of unique properties in comparison to conventional single-chain surfactants. They have much lower CMC values, higher surface activity, lower Kraft temperatures, better lime-soap dispersing properties and are often better wetting agents [20-24]. They are widely used as antifoaming agents, effective emulsifiers, dispersants, in enhanced oil recovery, for drug entrapment and release, in soil remediation and in the construction of high porosity materials [25-27].

In the present investigation an attempt will be made to the study of physicochemical properties of single and binary systems of some conventional ionic, non-ionic, gemini surfactants and their interaction with serum albumin proteins and also will study the effect of solvent on these surfactants.

(3) A BRIEF REVIEW OF THE WORK ALREADY DONE IN THE FIELD

Protein-surfactant interactions are usually dependent on the surfactant features. Most of the researchers have been focused on single-chain surfactants. More recently, the binding between proteins and dimeric surfactants has been discussed. With regard to proteins, bovine serum albumin (BSA) is one of the most extensively studied serum albumins. Besides, BSA and human serum albumin, which is an important transfer protein, are approximately 76% homologous and display a strictly conserved repeating pattern of disulfides. Therefore, study of the behavior of surfactants in the presence of BSA can contribute to pharmacokinetics and pharmacodynamics [28-30]. Interaction of proteins with surfactants have been extensively studied due to various application of their mixture in biosciences, food, cosmetics, drug delivery, detergents and biotechnological processes [31-32].

Gelamo et al. [33] showed the higher efficacy of cetyltrimethylammoniun chloride (CTAC) over sodium dodecyl sulfate (SDS) to unfold the bovine serum albumin (BSA) at pH 7. They found that at low SDS concentration, the protein conformation does not change but in presence of CTAC concentration some unfolding and aggregation of BSA take place. Similarly, Li et al. [34] investigated the interaction of BSA with cationic gemini and single chain surfactant. Chakraborty et al. [35] revealed physicochemical and conformational studies on BSA-surfactant interaction in aqueous medium. They found that although BSA-alkyltrimethylammonium bromide (ATAB) systems represent oppositely charged polyelectrolyte-surfactant system, the interaction profile using tensiometry and microcalorimetry are much simpler compared to a BSA-SDS system with similar charges. Kabir-ud-din et al. [36] studied the interaction of bovine, rabbit and porcine serum albumins with cetyltrimethylammonium bromide (CTAB) and gemini surfactant. They found that proteins undergo more significant unfolding with gemini as compare to CTAB.

Investigation of micellar and interfacial properties of surfactant mixtures has been the major objective of current research in surface chemistry. Extensive reviews on the micellization process of surfactants are available in literature [37-40]. Kabir-ud-Din and co-workers [41-43] studied the effect of solvent and temperature on self-aggregaion of some cationic dimeric surfactant by conductometric and fluorescence technique. Similarly the effect of alcohol on cationic surfactants have been studied by Sidima et al. [44]. Micellar and surface properties of some gemini and conventional surfactants investigated by Saha et al. [45-46]. He found that cationic gemini surfactants with a flexible and hydrophilic spacer are more attractive than the cationic gemini with rigid and less hydrophilic spacer.

Our research group studied the effect of additives in conventional monomeric and cationic gemini surfactants having different spacer chain lengths and also studied their mixed micellization behavior [47-50].

(4) OBJECTIVES

The main objectives of the proposed research work are as follows:

(I) Physicochemical studies of some cationic, anionic, nonionic and gemini surfactants by conductivity, surface tension and fluorescence method.

(II) To study the solvent effect on monomeric and gemini surfactants.

(III) Micellization properties of binary and ternary mixtures of cationic gemini and monomeric surfactants.

(IV) To study the interaction of monomeric and dimeric surfactants with serum albumin proteins.

(5) NOTEWORTHY CONTRIBUTION IN THE FIELD OF PROPOSED WORK

The proposal is designed to investigate the binding behavior between surfactants and protein. Protein-surfactant system is interesting to study the behavior of gemini surfactants as denaturants and as solubilizing agents for proteins and the influence on the assembly behavior caused by protein. It has important role in the application in drug delivery, cosmetics, foods and many more. The studies proposed in this work would contribute to a better understanding of the role of the molecular structures of surfactants in surfactant-protein interaction and therefore in the behavior of surfactants as denaturants.

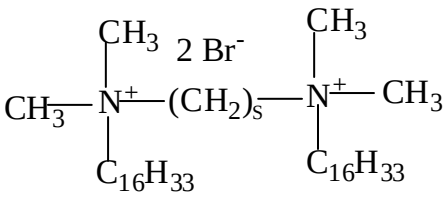
Much effort has been devoted in exploring the nature of micellization and surfactant behavior in polar organic solvents and solvent mixtures. Changing the solvent provides the opportunity to study the role of the so-called solvophobic effect as opposed to the hydrophobic effect in micellization.

(6) PROPOSED METHODOLOGY

The entire experimental work will be carried out in the following steps:

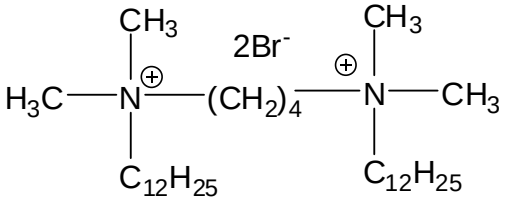
I. Micellar Characteristics of Some Monomeric and Cationic Gemini Surfactants

The micellar properties i.e. critical micelle concentration (CMC), aggregation number (N_{agg}), stern-volmer constant (K_{sv}), binding constant (K_S), interfacial and thermodynamic parameters of some cationic, anionic, nonionic and gemini surfactants (Scheme I) will be studied by conductivity, surface tension and fluorescence measurements.

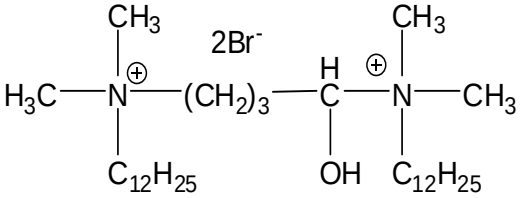


Alkanediyl-α,ω-bis(cetyldimethylammonium bromide)

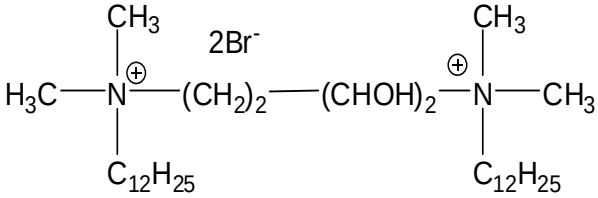
(C_{16}-s- C_{16},$2Br^-$ where s = 3, 4, 6, 10, 12)



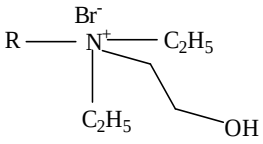
C_{12}-4-C_{12}, $2Br^-$



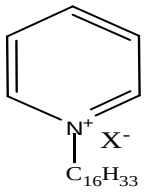
C_{12}-4 (OH)-C_{12}, $2Br^-$



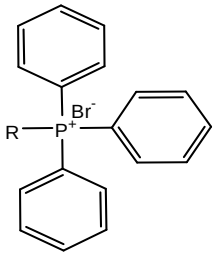
C_{12}-4$(OH)_2$-C_{12}, $2Br^-$



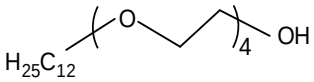
Alkyldiethylethanolammonium bromide
[R = $C_{16}H_{33}$ (CDEEAB), $C_{14}H_{29}$ (TDEEAB)]



Cetylpyridinium halide
X^- = Br^- (CPB)
X^- = Cl^- (CPC)



Alkyltriphenylphosphonium bromide
[R = $C_{16}H_{33}$ (CTPB), $C_{14}H_{29}$ (TTPB)]



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Scheme I Structure of some monomeric and gemini surfactants

II. Solvent Effect on Micellar Properties of Some Monomeric and Gemini Surfactants

The micellar, interfacial and thermodynamic properties of surfactants are dependent on environmental factors namely pH, temperature, pressure and additives, such as cosolvent, co-surfactants and added electrolytes. The interfacial and micellar properties of surfactant solutions are governed by solvophobic and solvophilic interactions. This effect can be changed by altering the nature of the amphihile as well as the nature of the bulk phase after addition of polar organic solvent. Different organic solvents i.e, dimethylsulfoxide (DMSO), dimethylformamide (DMF), ethanol (C_2H_5OH), acetonitrile (CH_3CN) and tetrahydrofuran (THF), formamide, ethylene glycol (EG), diethylene glycol (DEG), glycerol, 1,4 dioxane etc. will be used for the study of surfactant-solvent interaction.

III. Study of Mixed Micellization Behaviors of Binary and Ternary Mixture of Gemini and Cationic / Anionic / Nonionic Surfactants

Surfactant mixtures are known to have superior chemical and surface active properties over the individual surfactants, thereby requiring smaller amounts. To enhance the performance of surfactant mixtures further, it is helpful to understand the interaction among the surfactants. Surfactants interact in such a way that the critical micelle concentration (CMC) of the mixture falls in between (or below) the CMC's of individual components. The mixed micellization properties of binary and ternary mixture of gemini and cationic / anionic / nonionic surfactants will be evaluated by surface tension and conductivity method. The micellar compositions, activities and the mutual interactions of binary and ternary mixtures will be estimated by different theories (Clint, Rubingh, Rosen and Nagarajan model).

IV. Interaction of Cationic Monomeric and Dimeric Surfactants with Serum Albumin Proteins

Protein surfactant interactions depend on the structures of the protein and surfactant as well as their concentrations. One surfactant binds with protein it may either stabilize or destabilize the conformation of the protein and alter its function. It is important and interesting to study the behavior of surfactants with different chain lengths in the presence of serum albumin protein. An attempt will be made up to study the interaction of Bovine (BSA), Rabbit (RSA) and Porcine (PSA) serum albumin proteins with monomeric and dimeric surfactants by means of surface tension, conductivity, spectrofluorimetric and spectrophotometric techniques.

(7) EXPECTED OUTCOME OF THE PROPOSED WORK

Present work is aimed for the study of micellar characteristics by surface tension, conductivity and fluorescence measurements. Different solvents would have been used to study the role of the solvophobic effect on physicochemical properties and micellization process. The increasing use of novel surfactants in applications which require water-free media make this type of research more interesting and crucial due to novel technology requests. Micellar and interfacial properties in single and mixed surfactant system have been explore in this work to reveal the mixing behavior of surfactants.

The study of protein binding interaction could provide information about various factors on protein-surfactant interactions and also contribute to the understanding of the action of surfactant as solubilizing agents to recover proteins from inclusion bodies. Albumin have been used as model protein for many diverse biophysical, biochemical and physicochemical studies. The investigation provides interaction between protein and some gemini and monomeric surfactants as a model for molecular design and industrial research.

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(9) LIST OF THE PAPERS COMMUNICATED / SUBMITTED / PUBLISHED / IN JOURNALS / CONFERENCE / SYMPOSIUM

1. **Effect of Polar Organic Solvents on Self-Aggregation of Some Cationic Monomeric and Dimeric Surfactants**

   Srishti Dutta Roy and Kallol K. Ghosh, National Conference on Recent Trends in Chemical Sciences, January 23-25, 2014, Pt. Ravishankar Shukla University, Raipur (NCRTC-2014) (Presented).

2. **Micellization Behavior of Gemini Surfactants in Aqueous and Aquo-Organic Solvent Mixed Media**

   Srishti Dutta Roy, D. Tikariha and Kallol K. Ghosh, Recent Developments in Chemical Science & Technology:Young Scientists Meet, National Institute of Technology, Rourkela, Odisha, March 15-16, 2014 (Presented)

Signature of Supervisor

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